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Why does N-limitation persist in the world's marine waters?

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ABSTRACT

Primary production of vast regions of the world's estuarine, coastal and pelagic ocean waters is limited by availability of fixed nitrogen; this despite the fact that a highly diverse suite of microorganisms potentially capable of fixing N_2 (eubacteria and cyanobacteria), inhabit these waters. Theoretically, diazotrophs should supply the N needs to balance the N required to support primary production, assuming other key limiting nutrients, phosphorus and iron, are available and energy requirements are met. In practice however, N_2 fixation often does not meet ecosystem-scale N demands, even when these nutrients are replete. The problem lies with the fact that optimal rates of N_2 fixation are often controlled by additional environmental factors, including light and organic matter availability, turbulence, and high levels of dissolved oxygen which can suppress this process in N-deplete surface waters. In addition, rates of N loss via denitrification and anammox can exceed N_2 fixation and external N inputs on annual scales in coastal and pelagic waters, including those experiencing eutrophication. This creates a situation where chronic N limitation persists, even in the presence of anthropogenic nitrogen enrichment. Many aquatic ecosystems exhibit a perpetual "hunger" for fixed N to support primary and higher levels of production and this is likely to continue over forseeable biological and geologic timescales.

1. Introduction

A persistent biogeochemical feature of vast regions of the world's oceans is that primary production is nitrogen (N)-limited (Dugdale, 1967; Ryther and Dunstan, 1971; Capone et al., 2008); this despite the fact that microbially-mediated nitrogen (N_2) fixation may supply combined N (as NH_3) that can relieve this limitation (Fogg, 1942; Capone and Carpenter, 1982; Voss et al., 2011; Gruber, 2016; Gardner et al., 2017). Stoichiometry suggests that that N_2 fixation should supply cellular N needs as long as phosphorus (P) and micronutrient (especially iron (Fe)) supplies are readily available (Doremus, 1982; Smith, 1984; Tyrrell, 1999; Paerl, 1990). However, global patterns of N_2 fixation are complex and and not completely understood and it has been noted that there is local and larger-scale spatial variability between where biologically-mediated N_2 fixation and N loss processes, including denitrification and anammox (Gruber and Sarmiento, 1997; Moore et al., 2013; Weber and Deutsch, 2014; Somes and Oschlies, 2015). Geochemical evidence suggests that N-limited conditions have prevailed in a bulk (~70%) of the world's ocean basins in recent geological time (Berman-Frank et al., 2008), and in numerous freshwater and brackish habitats, including lakes, estuaries and coastal seas (e.g., Baltic Sea) (Guildford et al., 2003; Elser et al., 2007; Paerl and Piehler, 2008; Conley et al., 2009; Abell et al., 2010; Kolzau et al., 2014). Therefore, the question arises, why doesn't N_2 fixation compensate for N limitation when there is enough available P and Fe present to support this process?

The problem doesn't seem to be one of flawed stoichiometry, hidden or unrecognized sources of carbon and phosphorus that are left unexplained to balance the atomic "Redfield Ratio" of 106:16:1 (C:N:P) needed to achieve "optimal growth" of primary producers (Redfield, 1958), but rather an imbalance of supplies in these cellular constituents. There are highly diverse N_2 fixing Eubacterial, Archaeal, and Cyanobacterial communities present in marine and freshwater systems (Zehr et al., 2003; Zehr and Paerl, 2008). Here, I examine the array of environmental constraints and limitations that can help explain the apparent chronic discrepancy between N requirements and the ability of N_2 fixation to match them in aquatic ecosystems.

An assumption regarding environmental demands and controls of N_2 fixation is that N_2 fixation should supply the appropriate amount of nitrogen to support growth, if adequate amounts of biologically-available phosphorus are available (Doremus, 1982; Froelich, 1988; Tyrrell, 1999; Schindler et al., 2008). However, this balance is seldom achieved on either the organismal or the ecosystem level (Paerl, 1990; Scott and McCarthy, 2010; Lewis et al., 2011; Paerl et al., 2016). What is the reason for this shortfall?

The enzymatically-mediated (nitrogenase) process of N_2 fixation relies on adequate P, Fe and (in the case of micro-heterotrophs) organic C supplies. However, it also has a very high energy demand, requiring

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approximately 16 ATPs and at least 8 reducing equivalents (electrons) and protons to "fix" one molecule of N_2 in the following equation: N2 + 8H+ + 8e- + 16 ATP = 2NH3 + H2 + 16ADP + 16 Pi (Gallon, 1992). Light is the main energy source in phototrophic diazotrophs, including photosynthetic bacteria and cyanobacteria. By contrast, organic carbon compounds and redox reactions supply the energy and reductant needed to drive this process in non-cyanobacterial heterotrophic prokaryotes. Therefore, adequate sunlight to support photosynthesis and availability of oxidizable organic matter to support heterotrophy are required for this process to operate at maximal rates. In addition, the enzyme complex mediating N_2 fixation (dinitrogenase reductase) contains iron and molybdenum as cofactors, so adequate supplies of these metals in biologically-available forms is essential for the optimal function of this complex. Furthermore, energy transferring compounds, such as ferredoxin, NADH/NADPH require Fe and other metal cofactors (Co, others) to operate. Lastly, N_2 fixation is an evolutionarily "ancient" anaerobic process, which most likely evolved during the anoxic pre-Cambrian period (Towe et al., 2002). It is inactivated irreversibly in the presence of molecular oxygen (O_2) (Gallon, 1992), and experimental evidence indicates that the process is partially suppressed at pO_2 levels ranging from subsaturated to supersaturated, among a wide range of cyanobacteria (Paerl and Kellar, 1978; Fay, 1992; Gallon, 1981, 1992; Paerl, 2017). Vast stretches of the oceans that are most N-deplete are also fully oxygenated and at times supersaturated, and may exhibit Fe limitation (or co-limitation). The above requirements and constraints interact with P availability to control when, where and how much N_2 can be fixed in the global ocean as well as freshwater ecosystems (Fig. 1).

Diazotrophic microbes, especially cyanobacteria, the only oxygenic phototrophs capable of N_2 fixation, have developed diverse strategies for addressing the "oxygen problem" (Fay, 1992; Gallon, 1992). These factors include; 1) forming colonies and aggregates, which spatially separate photosynthesis and N_2 fixation (Paerl et al., 1988; Paerl and Bebout, 2018), 2) temporal separation of processes, with oxygenic photosynthesis supplying energy and carbon needs during daytime and conducting N_2 fixation at night (Paerl, 1990; Zehr and Paerl, 2008), 3) confining N_2 fixation to specialized, O_2-free cells called heterocysts during daytime (Fay, 1992; Wolk, 1996), and 4) participating in symbiotic relationships, either as endosymbionts or episymbionts, with eukaryotic algae (e.g., the Rhizoselenia-Richelia symbiosis), higher plants and invertebrates (Postgate, 1988; Kneip et al., 2007; Fiore et al., 2010; Foster et al., 2011).

These cellular and organismal adaptations constitute ingenious strategies for fixing N_2 in an "inhospitable" modern-day oxic biosphere (c.f., Postgate, 1988; Fay, 1992; Gallon, 1981, 1992; Kneip et al., 2007; Fiore et al., 2010). However, they are neither "perfect" nor 100% efficient in supplying the organismal needs for fixed N. In fact, even0020the most highly evolved heterocystous cyanobacteria are sensitive to inward oxygen diffusion during active growth or "bloom" periods, when ambient O_2 saturation readily exceeds 100% (pO2 ~ 0.2) (Stewart and Pearson, 1970; Fay, 1992; Gallon, 1981; Gallon, 1992; Wolk, 1996; Paerl, 1978; Paerl and Kellar, 1978; Paerl, 2017) (Fig. 2).

The capacity for N_2 fixing microorganisms to supply fixed N must be addressed at the ecosystem scale, in the context of net N fluxes and budgets. The main biogeochemical N loss mechanisms on this scale are denitrification, i.e. the conversion of NO_3^- to N_2 (Capone et al., 2008), volatilization of gaseous N forms, such as NH_3, N_2O, NO and NO_2 (Devol et al., 2006; Ward, 2007), anammox ((the anaerobic oxidation of ammonium and nitrite to N_2) (Dalsgaard et al., 2012), and burial (Gruber, 2008). Together, these processes represent significant within-system losses in freshwater, estuarine and coastal ecosystems. Denitrification is a major N loss pathway (Seitzinger, 1988; Seitzinger and Giblin, 1996; Joye et al., 1996; Codispoti et al., 2001; Grantz et al., 2014; Zhu et al., 2018), and where comparisons have been made more N appears to be leaving than entering when areal rates of N_2 fixation are compared to denitrification on an annual basis (Codispoti et al.,

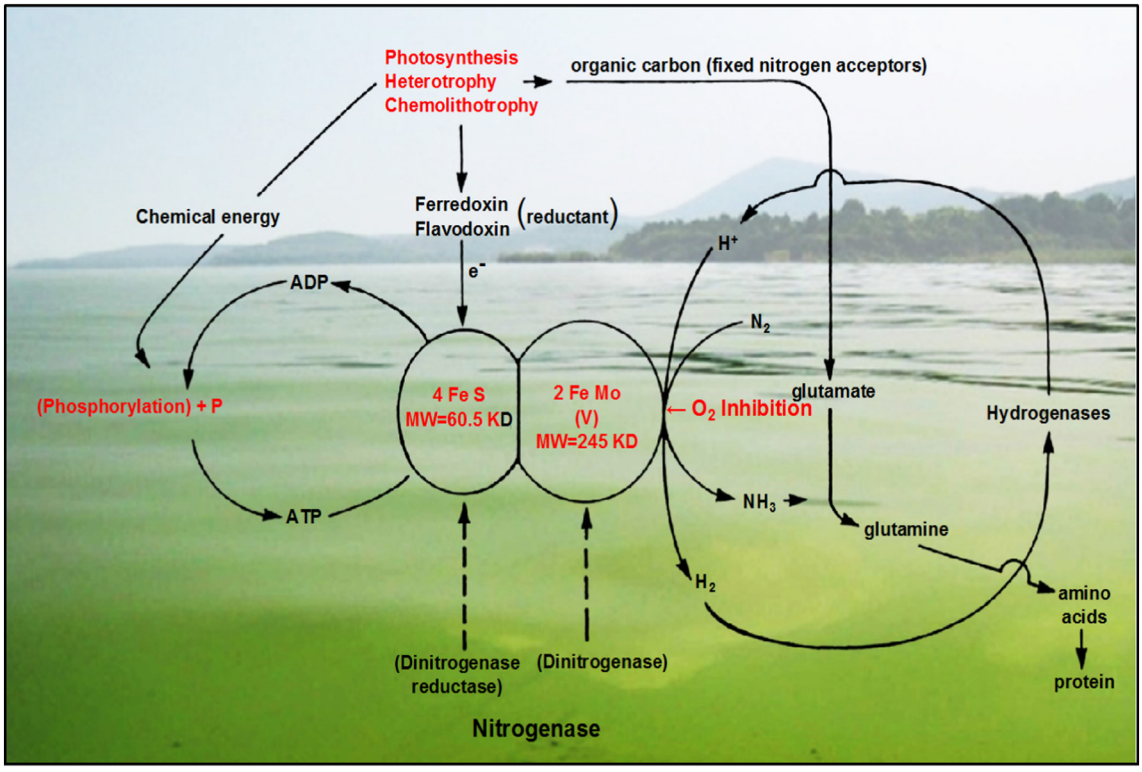

Fig. 1. The nitrogen fixing process, as mediated by cyanobacteria (utilizing oxygenic photosynthesis as an energy and C source), heterotrophic and chemolithotrophic microorganisms, in surface waters. Potential environmental controls, including phosphorus (P) and iron (Fe) availability, energy sources, and dissolved oxygen inhibition, are shown highlighted in yellow. Figure adapted from Paerl, 2017. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

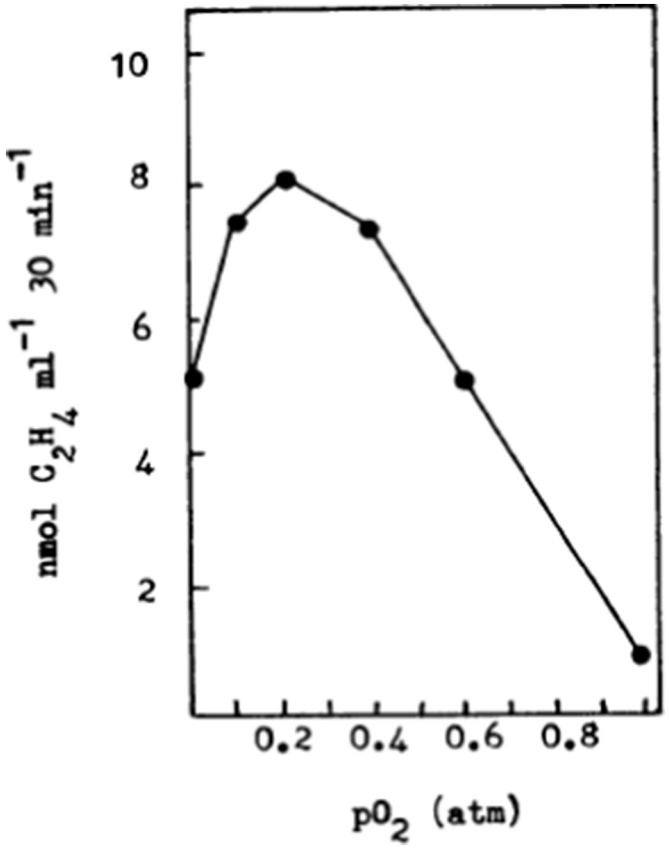

Fig. 2. Effect of dissolved oxygen saturation (pO_2) on nitrogenase activity (acetylene reduction) of *Anabaena flos-aquae*, incubated for 2 h under 3 klx irradiation. At 100% saturation, pO2 is ~ 0.2. Figure adapted with permission from Fay, 1992 and Stewart and Pearson, 1970.

2001; Gruber, 2008). Also, in eutrophic freshwater lakes harboring N_2 fixing cyanobacterial blooms, rates of denitrification invariably exceeded N_2 fixation rates on annual time scales (Paerl and Scott, 2010; Grantz et al., 2014; Paerl et al., 2016). Like aerobic respiration, anaerobic denitrification yields energy (ATP), while N_2 fixation has very high energy costs. Therefore, from an energetic balance perspective, denitrification is an energy-yielding process, while N_2 fixation is a significant energy-requiring process with light controlling autotrophic and organic matter controlling heterotrophic N_2 fixation. In highly turbid and/or colored waters, the availability of photosynthetically-active radiation can potentially control N_2 fixation rates among diazotrophic cyanobacterial taxa (Paerl, 1990).

Denitrification and anammox rates are often high and exceed "new" inputs via N_2 fixation when compared in sub-oxic oceanic regions (Devol et al., 2006; Ward, 2007; Codispoti et al., 2001; Dalsgaard et al., 2012) and in nutrient enriched coastal systems (Seitzinger, 1988; Herbert, 1999); although it must be cautioned that rates of these processes may vary substantially throughout the global ocean (Gruber, 2008). Oxygen minimum zones occur in diverse regions of the world's oceans (e.g., Indian Ocean, Eastern Pacific, coastal regions supporting hypoxic bottom waters). While these regions can at times exhibit significant rates of N_2 fixation per unit area, denitrification rates generally exceed those for N_2 fixation (Codispoti et al., 2001; Galloway et al., 2004; Gruber, 2008) (Table 1). Rates of denitrification and other intermediate N gas transformations (e.g., N_2O production) may increase in the Anthropocene, as eutrophication, and hence the availability of organic matter mediating these transformations, expands into the coastal ocean and beyond (Codispoti et al., 2001).

Studies in freshwater and marine systems undergoing accelerating eutrophication suggest increasing frequencies of N and P co-limitation

Table 1
Sources and sinks of fixed N in the marine environment. Table extracted from Gruber, 2008.

Process	Codispoti et al.[a]	Galloway et al.[a,b]	Gruber[a]
	Sources (Tg N yr^{-1})		
Pelagic N_2 fixation	117	106	120 ± 50
Benthic N_2 fixation	15	15	15 ± 10
River input (DON)	34	18[c]	35 ± 10
River input (PON)	42	30[c]	45 ± 10
Atmospheric deposition	86	33	50 ± 20
Total sources	294	202	265 ± 55
	Sinks (Tg N yr^{-1})		
Organic N export	1		1
Benthic denitrification	300	206	180 ± 50
Water column denitrification	150	116	65 ± 20
Sediment Burial	25	16	25 ± 10
N_2O loss to atmosphere	6	4	4 ± 2
Total sinks	482	342	275 ± 55

[a] See the original publication for details, i.e. Galloway et al. (2004), Codispoti et al. (2001) and Gruber (2008).
[b] Listed are the central values reported by Galloway et al. (2004) (see Table 1 and Fig. 1 of their publication).
[c] Galloway et al. (2004) lists only the total river flux. I assumed that about two thirds of the total is PON, and one third is DON.

and exclusive N limitation with increases in trophic state and P loading (Elser et al., 2007; Conley et al., 2009; Paerl and Scott, 2010; Grantz et al., 2014). This observation is attributed to denitrification rates increasing relative to N_2 fixation rates with organic matter enriched conditions as systems become more eutrophic (Paerl et al., 2016; Gardner et al., 2017).

Climatic changes may further exacerbate N-limited conditions in both freshwater and marine environments. Global warming enhances metabolic rates, including those mediating N transformations. This phenomena may affect denitrification more than N_2 fixation, because the former relies on temperature-sensitive organic matter oxidation/decomposition as a source of energy, while N_2 fixation in photoautotrophs relies more heavily on radiant energy. Studies at high latitudes (tundra as well as aquatic habitats) indicate mineralization of organic matter and respiration are highly temperature-dependent, whereas N_2 fixation rates are less dependent on these reactions (Postgate, 1998). Note, the former processes, critical to denitrification potential, are stimulated significantly by warming (Veraart et al., 2011; Keil et al., 2015).

More extreme episodic rainfall events as well as a generally wetter climate appear symptomatic of climatic changes taking place in many regions in Earth. This leads to increased nutrient and organic matter runoff and inputs to estuarine, coastal and pelagic regions (Hilton et al., 2008; IPCC, 2014; Regnier et al., 2014; Tian et al., 2015; Raymond et al., 2016). These factors stimulate not only eutrophication, but also intensify salinity stratification in surface waters, which combined enhance the production and expansion of low oxygen "dead zone" bottom waters (Diaz and Rosenberg, 2008). This pattern will expand habitats ideal for denitrification far more than N_2 fixation (McCarthy et al., 2015), which can be suppressed by elevated concentrations of ammonium in such low oxygen habitats; further offsetting the balance between these processes in favor of denitrification. It is difficult to envision a scenario where the opposite effects can be expected, in part because the anticipated microbial habitat conditions favor denitrification and the increases in anthropogenic nitrate and other combined N loadings accompanying eutrophication will tend to suppress N_2 fixation rates (Postgate, 1998).

With increases in anthropogenic external nutrient, and specifically N, loadings to the biosphere (Galloway et al., 2002) and anticipated increases in episodic rainfall and runoff as well as groundwater discharge events accompanying climatic changes (Trenberth, 2011), why

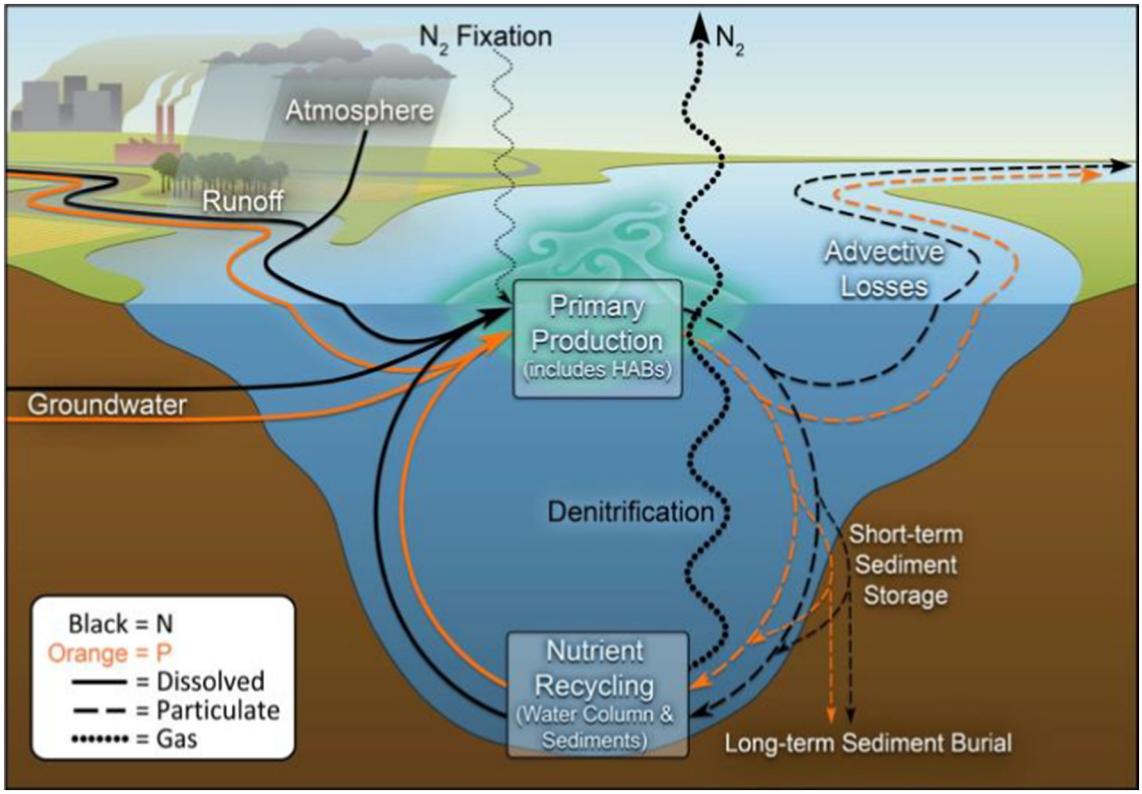

Fig. 3. Conceptual diagram, illustrating nitrogen (N) and phosphorus (P) inputs, outputs and storage in aquatic ecosystems. Note that only N has gaseous forms (dotted lines) that can exchange with the atmosphere. In systems with a history of excessive N and P loading, N limitation is perpetuated because there is more N "lost" via denitrification than gained by N2 fixation. Figure adapted from Paerl et al., 2016.

would N limitation not be relieved in receiving marine waters? Increased N (dominated by nitrate) loading will accelerate estuarine and coastal eutrophication, leading to an increase in autochthonous organic matter production (Paerl and Piehler, 2008; Jessen et al., 2015). Increased terrestrial (allochthonous) runoff will increase organic matter input from impacted watersheds, stimulating heterotrophic activity. Furthermore, increased freshwater discharge will enhance vertical density stratification in receiving estuarine and coastal waters. The combined effects of increased nitrate and organic matter enrichment and stronger stratification include promotion of bottom water hypoxia and denitrification, with less of a positive (if any) effect on N_2 fixation. Phosphorus enrichment also occurs in this scenario, but since there's no gaseous form of P that can 'escape' the system, P exhibits high retention rates on the ecosystem scale (Vollenweider, 1975; Kennedy, 1999). Hence, P continues to accumulate and internally cycle, thereby minimizing P-limitation and further promoting denitrification. This scenario is depicted in the following figure (Fig. 3; adapted from Paerl et al., 2016). In effect, the somewhat counter-intuitive scenario that evolves is one of estuarine and coastal waters becoming chronically "nitrogen hungry" as they receive increasing doses of both anthropogenic nitrogen (a large fraction of it nitrate) and organic matter, both of which would stimulate denitrification and other N loss mechanisms (anammox, volatilization of gaseous N forms) to a greater extent than N_2 fixation.

2. Concluding remarks

Given the evolutionary biogeochemical "bottleneck" created by a modern-day oxic biosphere, combined with increasing anthropogenic and climatic pressures tending to favor denitrification over N_2 fixation, it seems likely that the global oceans as well as most inland waters will continue to be characterized as being chronically N deficient or "limited"; this despite the fact that N emissions and discharge to these waters are likely to continue increasing with human population growth, expanding agricultural and industrial production and urbanization. This paradox will continue in the near future as a fixed nitrogen "glut" continues. Complicating this scenario is the increased generation of N-based greenhouse gases (e.g., N_2O, NO_x) from human generation and discharge of fixed N compounds, which modulate our climate (Zaehle et al., 2011; Suddick et al., 2013). Ironically, this pattern seems to create a positive feedback loop. The more we create and disperse fixed N in the biosphere, the greater the denitrification potential, while N_2 fixation potentials are either unaffected or reduced. This would lead to an increased disparity between biologically-mediated inputs and outputs of fixed N and the maintenance of N limited conditions. There are exceptions to this in the case of very large anthropogenic N inputs, such as reported in freshwater and marine waters impacted by excessive anthropogenicaly-generated terrigenous and atmospheric N inputs (Elser et al., 2009; Yang and Gruber, 2016). A specific example includes Lake Tahoe, CA-NV, where sharp increases in atmospheric N loading from fossil fuel emissions in the Tahoe Basin has shifted the lake from exclusively N limited lake up to the 1970's to one that is now N and P co-limited (Jassby et al., 1994). Another example is the effect of the spring, N-rich runoff period in the Mississippi plume region of the northern Gulf of Mexico, that has driven these waters into periodic P limitation (Sylvan et al., 2006). However, even in this extreme case, the system returns to N limited conditions during much of the rest of the year (Justić et al., 1995).

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References

Abell, J.M., Özkundakci, D., Hamilton, D.P., 2010. Nitrogen and phosphorus limitation of phytoplankton growth in New Zealand lakes: implications for eutrophication control. Ecosystems 13, 966–977.

Berman-Frank, I., Chen, Y.-B., Gao, Y., Fennel, K., Follows, M.J., Milligan, A.J., Falkowski, P.G., 2008. Feedbacks between the nitrogen, carbon and oxygen cycles. Pp. 1537–1563. In: Capone, D.G., Mulholland, M., Carpenter, E. (Eds.), Nitrogen in the Marine Environment. vol. 2 Academic Press, Orlando.

Capone, D.G., Carpenter, E.J., 1982. Nitrogen fixation in the marine environment. Science 2017, 1140–1142.

Capone, D.G., Mulholland, M., Carpenter, E.J. (Eds.), 2008. Nitrogen in the Marine Environment. 2 Academic Press, Orlando.

Codispoti, L.A., Brandes, J.A., Christensen, J.P., Devol, A.H., Naqvi, S.W.A., Paerl, H.W., Yoshinari, T., 2001. The oceanic fixed nitrogen and nitrous oxide budgets: moving targets as we enter the anthropocene? Sci. Mar. 65, 85–105 Supp. 2.

Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Controlling eutrophication: nitrogen and phosphorus. Science 323, 1014–1015.

Dalsgaard, T., Thamdrup, B., Farías, L., Revsbech, N.P., 2012. Anammox and denitrification in the oxygen minimum zone of the Eastern South Pacific. Limnol. Oceanogr. 57, 1331–1346.

Devol, A.H., Uhlenhopp, A.G., Naqvi, S.W.A., Brandes, J.A., Jayakumar, D.A., Naik, H., Gaurin, S., Codispoti, L.A., Yoshinari, T., 2006. Denitrification rates and excess nitrogen gas concentrations in the Arabian Sea oxygen deficient zone. Deep-Sea Res. 53, 1533–1547.

Diaz, R.J., Rosenberg, R., 2008. Spreading dead zones and consequences for marine ecosystems. Science 321, 926–929.

Doremus, C., 1982. Geochemical control of dinitrogen fixation in the open ocean. Biol. Oceanogr. 1, 429–436.

Dugdale, R.C., 1967. Nutrient limitation in the sea: dynamics, identification, and significance. Limnol. Oceanogr. 12, 685–695.

Elser, J.J., Bracken, M.E.S., Cleland, E.E., Gruner, D.S., Harpole, W.S., Hillebrand, H., Bgai, J.T., Seabloom, E.W., Shurin, J.B., Smith, J.E., 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. Ecol. Lett. 10, 1124–1134.

Elser, J.J., Andersen, T., Baron, J.S., Bergström, A.-K., Jansson, M., Kyle, M., Nydick, K.R., Steger, L., Hessen, D.O., 2009. Shifts in lake N:P stoichiometry and nutrient limitation driven by atmospheric nitrogen deposition. Science 326, 835–836. https://doi.org/10.1126/science.1176199.

Fay, P., 1992. Oxygen relations of nitrogen fixation in cyanobacteria. Microbiol. Rev. 56, 340–373.

Fiore, C.L., Jarrett, J.K., Olson, N.D., Lesser, M.P., 2010. Nitrogen fixation and nitrogen transformations in marine symbioses. Trends Microbiol. 18, 455–463.

Fogg, G.E., 1942. Studies on nitrogen fixation by blue-green algae. J. Exp. Biol. 19, 78–87.

Foster, R.A., Kuypers, M.M., Vagner, T., Paerl, R.W., Musat, N., Zehr, J.P., 2011. Nitrogen fixation and transfer in open ocean diatom–cyanobacterial symbioses. ISME J. 5, 1484–1493.

Froelich, P.N., 1988. The problem with phosphorus. Eos 69, 760–761.

Gallon, J.R., 1981. The oxygen sensitivity of nitrogense: a problem for biochemists and micro-organisms. Trends Biochem. Sci. 6, 19–23.

Gallon, J.R., 1992. Reconciling the incompatible—N_2 fixation and O_2. New Phytol. 122, 571–609.

Galloway, J.N., Cowling, E.B., Seitzinger, S.P., Sokolow, R.H., 2002. Reactive nitrogen: too much of a good thing. Ambio 31, 60–66.

Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., et al., 2004. Nitrogen cycles: past, present, future. Biogeochemistry 70, 153–226.

Gardner, W.S., Newell, S.E., McCarthy, M.J., Hoffman, D.K., Lu, K., Lavrentyev, P.J., Hellweger, F.L., Liu, Z., Bruesewitz, D.A., Paerl, H.W., 2017. Community biological ammonium demand: a conceptual model for blooms in eutrophic lakes. Environ. Sci. Technol. 51, 7785–7793. https://doi.org/10.1021/acs.est.6b06296.

Grantz, E.M., Haggard, B.E., Scott, J.T., 2014. Stoichiometric imbalance in rates of nitrogen and phosphorus retention, storage, and recycling can perpetuate nitrogen deficiency in highly-productive reservoirs. Limnol. Oceanogr. 59, 2203–2216.

Gruber, N., 2008. The marine nitrogen cycle: Overview and challenges. Pp. 1–50. In: Capone, D.G., Mulholland, M., Carpenter, E. (Eds.), Nitrogen in the Marine Environment. vol. 2 Academic Press, Orlando.

Gruber, N., 2016. Elusive marine nitrogen fixation. Proc. Natl. Acad. Sci. U. S. A. 113 (16), 4246–4248.

Gruber, N., Sarmiento, J.L., 1997. Global patterns of marine nitrogen fixation and denitrification. Glob. Biogeochem. Cycles 11, 235–266.

Guildford, S.J., Hecky, R.E., Taylor, W.D., Mugidde, R., Bootsma, H.A., 2003. Nutrient enrichment experiments in tropical Great Lakes Malawi/Nyasa and Victoria. J. Great Lakes Res. 29, 89–106.

Herbert, R.A., 1999. Nitrogen cycling in coastal marine ecosystems. FEMS Microbiol. Rev. 23, 563–590.

Hilton, R.G., Galy, A., Hovius, N., Chen, M.-C., Horng, M.-J., Chen, H., 2008. Tropical-cyclone-driven erosion of the terrestrial biosphere from mountains. Nat. Geosci. 1, 759–762.

Jassby, A.D., Reuter, J.E., Axler, R.P., Goldman, C.R., Hackley, S.H., 1994. Atmospheric deposition of nitrogen and phosphorus in the annual nutrient load of Lake Tahoe (California-Nevada). Wat. Res. Res. 30, 2207–2216. https://doi.org/10.1029/94WR00754.

Jessen, C., Bednarz, V., Rix, L., Teichberg, M., Wild, C., 2015. Marine eutrophication. In: Armon, R.H., Hänninen, O. (Eds.), Environ. Indic. 27. Springer, Berlin. https://doi.org/10.1007/978-94-017-9499-2_11.

Joye, S.B., Smith, S.V., Hollibaugh, J.T., Paerl, H.W., 1996. Estimating denitrification rates in estuarine sediments: a comparison of stoichiometric and acetylene based methods. Biogeochemistry 33, 197–215.

Justić, D., Rabalais, N.N., Turner, R.E., Dortch, Q., 1995. Changes in nutrient structure of river-dominated coastal waters: Stoichiometeric nutrient balance and its consequences. Estuar. Coast. Shelf Sci. 40, 339–356.

Keil, D., Niklaus, P.A., von Riedmatten, R.L., Boeddinghaus, R.S., Dormann, C.F., Scherer-Lorenzen, M., Kandeler, E., Marhan, S., 2015. Effects of warming and drought on potential N_2O emissions and denitrifying bacteria abundance in grasslands with different land-use. FEMS Microb. Ecol. 91, fiv066. https://doi.org/10.1093/femsec/fiv066.

Kennedy, R.H., 1999. Basin-wide considerations for water quality management: importance of phosphorus retention by reservoirs. Int. Rev. Hydrobiol. 84, 557–566.

Kneip, C., Lockhart, P., Voß, C., Maier, U.-G., 2007. Nitrogen fixation in eukaryotes – New models for symbiosis. BMC Evol. Biol. 7, 55. https://doi.org/10.1186/1471-2148-7-55.

Kolzau, S., Wiedner, C., Rücker, J., Köhler, J., Köhler, A., Dolman, A.M., 2014. Seasonal patterns of nitrogen and phosphorus limitation in four German lakes and the predictability of limitation status from ambient nutrient concentrations. PLoS ONE 9 (4), e96065. https://doi.org/10.1371/journal.pone.

Lewis, W.M., Wurtsbaugh, W.A., Paerl, H.W., 2011. Rationale for control of anthropogenic nitrogen and phosphorus in inland waters. Environ. Sci. Technol. 45, 10030–10035.

McCarthy, M.J., Newell, S.E., Carini, S.A., Gardner, W.S., 2015. Denitrification dominates sediment nitrogen removal and is enhanced by bottom-water hypoxia in the northern Gulf of Mexico. Estuar. Coasts 38, 2279–2294.

Moore, C.M., Mills, M.M., Arrigo, K.R., Berman-Frank, I., Bopp, L., Boyd, P.W., Galbraith, E.D., Geider, R.J., Guieu, C., Jaccard, S.L., Jickells, T.D., La Roche, J., Lenton, T.M., Mahowald, N.M., Marañón, E., Marinov, I., Moore, J.K., Nakatsuka, T., Oschlies, A., Saito, M.A., Thingstad, T.F., Tsuda, A., Ulloa, O., 2013. Processes and patterns of oceanic nutrient limitation. Nature Geosc. 6, 601–610.

Paerl, H.W., 1978. Light-mediated recovery of N_2 fixation in the blue-green algae Anabaena spp. in O_2 supersaturated waters. Oecologia (Berl.) 32, 135–139.

Paerl, H.W., 1990. Physiological ecology and regulation of N_2 fixation in natural waters. Adv. Microb. Ecol. 11, 305–344.

Paerl, H.W., 2017. The cyanobacterial nitrogen fixation paradox in natural waters. F1000 Faculty Rev. 6, 244. https://doi.org/10.12688/f1000research.10603.1.

Paerl, H.W., Bebout, B.M., 2018. Direct measurement of O_2-depleted microzones in marine Oscillatoria: Relation to N_2 fixation. Science 241, 442–445 (1988).

Paerl, H.W., Kellar, P.E., 1978. Significance of bacterial (Cyanophyceae) Anabaena associations with respect to N_2 fixation in freshwater. J. Phycol. 14, 254–260.

Paerl, H.W., Piehler, M.F., Capone, D.G., Mulholland, M., 2008. Nitrogen and marine eutrophication. pp 529–567. In: Carpenter, E. (Ed.), Nitrogen in the Marine Environment. Vol. 2 Academic Press, Orlando.

Paerl, H.W., Scott, J.T., 2010. Throwing fuel on the fire: synergistic effects of excessive nitrogen inputs and global warming on harmful algal blooms. Environ. Sci. Technol. 44, 7756–7758.

Paerl, H.W., Bebout, B.M., Prufert, L.E., 1988. Physiological ecology and environmental control of N_2 fixation in marine and freshwater microbial associations. pp. 711-716. In: Bothe, H. (Ed.), Proc. 7th Intl. Congress on N_2 Fixation, Cologne, W. Germany. Springer Verlag, W. Germany.

Paerl, H.W., Scott, J.T., McCarthy, M.J., Newell, S.E., Gardner, W.S., Havens, K.E., Hoffman, K., Wilhelm, S.W., Wurtsbaugh, W.A., 2016. It takes two to tango: when and where dual nutrient (N & P) reductions are needed to protect lakes and downstream ecosystems. Environ. Sci. Technol. 50, 10805–10813.

Postgate, J., 1998. Nitrogen Fixation, 3rd ed. Cambridge University Press, Cambridge.

Raymond, P.A., Saiers, J.E., Sobczak, W.V., 2016. Hydrological and biogeochemical controls on watershed dissolved organic matter transport: pulse-shunt concept. Ecology 95, 833–844.

Redfield, A.C., 1958. The biological control of chemical factors in the environment. Am. Sci. 46, 205–222.

Regnier, P., Lauerwald, R., Ciais, P., 2014. Carbon leakage through the terrestrial-aquatic Interface: implications for the Anthropogenic CO2 Budget. Proced. Earth Plan. Sci. 10, 319–324.

Ryther, J.H., Dunstan, W.M., 1971. Nitrogen, phosphorus, and eutrophication of the coastal marine environment. Science 171, 1009–1013.

Schindler, D.W., Hecky, R.E., Findlay, D.L., Stainton, M.P., Parker, B.R., Paterson, M., Beaty, K.G., Lyng, M., Kasian, S.E.M., 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year wholeecosystem experiment. Proc. Natl. Acad. Sci. U. S. A. 105 (32), 11254–11258.

Scott, J.T., McCarthy, M.J., 2010. Nitrogen fixation may not balance the nitrogen pool in lakes over timescales relevant to eutrophication management. Limnol. Oceanogr. 55, 1265–1270.

Seitzinger, S.P., 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnol. Oceanogr. 33, 702–724.

Seitzinger, S.P., Giblin, A.E., 1996. Estimating denitrification in North Atlantic continental shelf sediments. Biogeochemistry 35, 235–259.

Smith, S.V., 1984. Phosphorus versus nitrogen limitation in the marine environment. Limnol. Oceanogr. 29, 1149–1160.

Somes, C.J., Oschlies, A., 2015. On the influence of 'non-Redfield' dissolved organic nutrient dynamics on the spatial distribution of N2 fixation and the size of the marine fixed nitrogen inventory. Glob. Biogeochem. Cycles 29, 973–993. https://doi.org/10.1002/2014GB005050.

Stewart, W.D.P., Pearson, H.W., 1970. Effect of aerobic and anaerobic conditions on growth and metabolism of blue-green algae. Proc. R. Soc. London, Ser. B 175, 293–311.
Suddick, E., Whitney, P., Townsend, A.R., Davidson, E.A., 2013. The role of nitrogen in climate change and the impacts of nitrogen–climate interactions in the United States: foreword to thematic issue. Biogeochemistry 1-10 (1), 114. https://doi.org/10.1007/s10533-012-9795-z.
Sylvan, J.B., Dortch, Q., Nelson, D.M., Maier-Brown, A.F., Morrison, W., Ammerman, J.W., 2006. Phosphorus limits phytoplankton growth on the Louisiana shelf during the period of hypoxia formation. Environ. Sci. Technol. 40, 7548–7553.
Tian, H., Yang, Q., Najjar, R.G., Ren, W., Friedrichs, M.A.M., Hopkinson, C.S., Pan, S., 2015. Anthropogenic and climatic influences on carbon fluxes from eastern North America to the Atlantic Ocean: a process-based modeling study. J. Geophys. Res. Biogeosci. 120, 757–772.
Towe, K.M., Berman-Frank, I., Falkowski, P.G., 2002. Evolution of nitrogen fixation. Science 295, 798–799.
Trenberth, K., 2011. Changes in precipitation with climage change. Clim. Res. 47, 123–138.
Tyrrell, T., 1999. The relative influences of nitrogen and phosphorus on oceanic primary production. Nature 400, 525–531.
Veraart, A.J., de Klein, J.J.M., Scheffer, M., 2011. Warming can boost denitrification disproportionately due to altered oxygen dynamics. PLoS ONE 6 (3), e18508. https://doi.org/10.1371/journal.pone.0018508.
Vollenweider, R.A., 1975. Input- output models with special reference to the phosphorus loading concept in limnology. Schweiz. Zeitsch. Hydrobiol. 37, 53–84.
Voss, M., Bange, H.W., Dippner, J.W., Middelburg, J.J., Montoya, J.P., Ward, B., 2011. The marine nitrogen cycle: recent discoveries, uncertainties and the potential relevance of climate change. Philos. Trans. R. Soc. B 368, 20130121. https://doi.org/10.1098/rstb.2013.0121.
Ward, B.B., 2007. What's new in the nitrogen cycle. Oceanography 20, 101–109.
Weber, T., Deutsch, C., 2014. Local versus basin-scale limitation of marine nitrogen fixation. Proc. Natl. Acad. Sci. U. S. A. 111, 8741–8746. https://doi.org/10.1073/pnas.1317193111.
Wolk, C.P., 1996. Heterocyst formation. Annu. Rev. Genet. 30, 59–78.
Yang, S., Gruber, N., 2016. The anthropogenic perturbation of the marine nitrogen cycle by atmospheric deposition: nitrogen cycle feedbacks and the 15N Haber-Bosch effect. Glob. Biogeochem. Cycles 30, 1418–1440. https://doi.org/10.1002/2016GB005421.
Zaehle, S.P., Ciais, A.D., Friend, R., Prieur, V., 2011. Carbon benefits of anthropogenic reactive nitrogen offset by nitrous oxide emissions. Nat. Geosci. 4, 601–605.
Zehr, J.P., Paerl, H.W., 2008. Molecular ecological aspects of nitrogen fixation in the marine environment. In: Kirchman, D. (Ed.), Microbial Ecology of the Oceans. Academic Press, New York, pp. 481–525.
Zehr, J.P., Jenkins, B.D., Short, S.M., Steward, G.F., 2003. Nitrogenase gene diversity and microbial community structure: a cross-system comparison. Environ. Microbiol. 5, 539–554.
Zhu, W., Wang, C., Hill, J., He, Y., Tao, B., Mao, Z., Wu, W., 2018. A missing link in the estuarine nitrogen cycle?: coupled nitrification-denitrification mediated by suspended particulate matter. Nat. Sci. Rep. 8, 2282. https://doi.org/10.1038/s41598-018-20688-4.